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Abstract

Regular eruptions from Sakurajima volcano, Japan, repeatedly cover local urban areas with volcanic ash. The frequency of exposure of local populations to the ash led to substantial concerns about possible respiratory health hazards, resulting in many epidemiological and toxicological studies being carried out in the 1980s. However, very few mineralogical data were available for determination of whether the ash was sufficiently fine to present a respiratory hazard. In this study, we review the existing studies and carry out mineralogical, geochemical and toxicological analyses to address whether the ash from Sakurajima has the potential to cause respiratory health problems. The results show that the amount of respirable (< 4 μm) material produced by the volcano is highly variable in different eruptions (1.1-18.8 vol. %). The finest samples derive from historical, plinian eruptions but considerable amounts of respirable material were also produced from the most recent vulcanian eruptive phase (since 1955). The amount of cristobalite, a crystalline silica polymorph which has the potential to cause chronic respiratory diseases, is ~3-5 wt. % in the bulk ash. SEM and TEM imaging showed no fibrous particles similar to asbestos particles. Surface reactivity tests showed that the ash did not produce significant amounts of highly reactive hydroxyl radicals (0.09-1.35 μmol m^{-2} at 30 mins.) in comparison to other volcanic ash types. A basic toxicology assay to assess the ability of ash to rupture the membrane of red blood cells showed low propensity for haemolysis. The findings suggest that the potential health hazard of the ash is low, but exposure and respiratory conditions should still be monitored given the high frequency and durations of exposure.

Keywords

Sakurajima; Japan; volcanic ash; health; respiratory; characterisation

Introduction

Sakurajima volcano, on Kyushu Island, SE Japan, is one of the most active volcanoes in Japan. Frequent, vulcanian-style eruptions have been occurring almost continuously for over half a century, regularly exposing local populations (almost 1 million inhabitants within a 10 km radius of the volcano) to volcanic ash. Since the late 1970s, concerns have been raised about how repeated exposure to volcanic ash over such a long timescale might affect the respiratory health of those exposed (Samukawa et al. 2003). Many epidemiological and toxicological studies were carried out, especially during the 1980s, to try to assess the pathogenicity of the ash. The studies gave a range of conclusions from toxic to inert (see below and Table 1) depending on study design, and the ambiguity within the literature has never been resolved. Detailed examination of the characteristics of the ash itself can help assess the potential for the ash to pose a respiratory health hazard. Key mineralogical analyses, such as grain-size distribution, were not examined in sufficient detail within the medical studies, leading to a lack of basic information such as whether the ash was actually inhalable.

Recent analyses of ash from several volcanoes (e.g. Vesuvius, Chaitén, Rabaul and Eyjafjallajökull) have led to a greater understanding about the respiratory health hazards posed by volcanoes, although many uncertainties still remain (Horwell et al. 2010a; Horwell et al. 2010b; Le Blond et al. 2010). After the most recent publication on the toxicity of ash from Sakurajima volcano (Samukawa et al. 2003), the volcano experienced a period of low activity, so concerns were eased but, in 2009, intense volcanic activity began once again. Advancements in knowledge and methods over recent years mean that mineralogical-based assessments can now be used to inform medical risk assessments (Horwell and Baxter 2006).

Here, we use mineralogical, geochemical and toxicological analyses on a range of samples, reflecting past and current styles of activity, to address whether the ash from Sakurajima volcano has the potential to cause respiratory disease. We employ an existing protocol (Le Blond et al. 2010), developed to rapidly examine the physico-chemical properties of volcanic ash, with results giving an indication of the potential for volcanic ash to cause acute or chronic respiratory problems, which can inform further study. The results provide a basis for rapid hazard mitigation at the onset of new eruptions of Sakurajima volcano and resolve some of the disparities within the literature. Results of this study can also contribute to future medical assessments and a growing global inventory of data on volcanic ash and respiratory health studies.

Potentially hazardous ash characteristics

A comprehensive summary of the respiratory health hazards posed by volcanic ash can be found in Horwell and Baxter (2006). Of particular concern at Sakurajima volcano is the possible presence of cristobalite, a crystalline silica polymorph similar to quartz, which may cause fibrosis in the lungs leading to silicosis after prolonged and heavy exposure (NIOSH 2002). Cristobalite is of concern at Sakurajima as a small lava dome or 'cap' is thought to form in the crater before vulcanian eruptions. The principal mechanisms of cristobalite formation in volcanoes are via vapour-phase deposition and devitrification of volcanic glass in lava domes (Baxter et al. 1999; Horwell et al. Submitted) which can occur on a time-scale of hours to days following emplacement of dome lava (Williamson et al. 2010). Reich et al. (2009) discovered nano-fibres of cristobalite in ash from explosive eruptions at Chaitén volcano in 2008, which are of concern due to their potential similarity to asbestiform minerals (Horwell and Baxter 2006). They proposed a new mechanism of cristobalite

formation, through a high-temperature reaction of amorphous silica with carbon monoxide in the explosion column, which should also be considered here.

Iron-catalysed reactions may also provide a pathway for toxicity. Harmful free radicals may be produced in the lungs by the Fenton reaction which generates the hydroxyl radical from ferrous iron on the surface of ash particles (Fubini et al. 1995).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet \qquad \text{(Eq. 1)}$$

Studies using volcanic ash have shown that available iron species on the surface of volcanic ash samples have the potential to generate substantial quantities of hydroxyl radicals (Horwell et al. 2007; Horwell et al. 2003a; Horwell et al. 2010b; Le Blond et al. 2010), although whether it is possible for volcanic ash to damage lung cells via this mechanism is still unknown.

However, the most pertinent ash characteristic to assess when examining potential health hazards is the grain-size distribution. If particles are too large to enter the lung, then they cannot pose a respiratory health hazard and, conversely, the finer the particles, the deeper into the lung they can penetrate (Horwell 2007). In general, particles deposited in the upper airways (< 100 μm, the 'inhalable' fraction) may cause irritation, whilst those deposited in the upper lungs (< 10 μm, the 'thoracic' fraction) may be involved with acute attacks of asthma and bronchitis in susceptible people. Of particular concern are particles deposited in the alveolar, gas exchange region of the lung (< 4 μm, the 'respirable' fraction) that are known, in occupational settings, to cause severe diseases such as lung cancer and silicosis, although their pathogenicity is determined by additional factors such as particle composition and solubility. Health-pertinent grain-size distributions can be measured rapidly and accurately by laser diffraction or can be estimated by sieving to 63 μm cut-off and then

applying the equation given by Horwell (2007). This allows immediate information to be gained on the potential inhalability of the ash so that mitigation measures can be put in place, such as distribution of dust masks.

Horwell (2007) published grain-size results for a single sample from Sakurajima volcano, erupted in January 1994 during a vulcanian explosion, but described by its collector as coming from an existing dome. This sample contained < 1 vol. % sub-4 μm material, a value which is particularly low compared to ~ 11 vol. % typical for dome-collapse ash and ~ 6 vol. % typical for vulcanian explosions from volcanoes such as the Soufrière Hills volcano, Montserrat (Horwell 2007). This result presented the possibility that ash from Sakurajima volcano could be too coarse to be a significant health hazard, and the current study aims to show whether the range of eruptive products from Sakurajima maintains this characteristic.

Geological Setting

Sakurajima is located in Kagoshima prefecture, Kyushu Island, south-eastern Japan, on the southern rim of the Aira Caldera (Figure 1). Kagoshima city encompasses Sakurajima volcano but most of its 600,000 citizens live ~10 km west of Sakurajima across the bay, with approximately 5,000 people living on the Sakurajima peninsula. Around 17,000 people also live in Tarumizu city to the southeast of the crater. Sakurajima consists of two adjoining stratovolcanoes, of which only the southern crater (Minamidake) and side vent (Showa) are active.

Historical eruptions at the volcano have been recorded since the 8th century (Kobayashi et al. 2007). Since 1471, five main eruptive phases have taken place: 1471-1476 (Bunmei era), 1779-1785 (An-ei era), 1914 (Taisho era), 1946 (Showa era) and the most recent phase

which began in 1955 (Kobayashi et al. 2007). Each eruptive phase was characterised by a number of explosive eruptions, initially ejecting large amounts of pyroclastic material and ash, followed by effusive lava flows from lateral fissure vents on the flanks of Minamidake summit (Fukuyama and Ono 1981). The largest historical eruptions were plinian eruptions in 1914 (VEI 4) and 1471-76 (VEI 5) where explosive activity generated large quantities of pumice (see Figure 2). Decreases in the SiO_2 wt. % with time, among the major historical eruptions, have been attributed to a coupled magma chamber system and magma mixing (Durand et al. 2001).

The current eruptive phase has been characterised by intermittent, but frequent, vulcanian-style eruptions from the summit Minamidake crater. After a period of relatively low activity since 2001, the frequency of explosive eruptions leapt from < 80 eruptions/year to 755 eruptions in 2009, 1026 eruptions in 2010 and 1227 eruptions for 2011 (until 12 December; http://www.jma-net.go.jp/kagoshima/vol/data/skr_erp_num.html). Over 8,000 individual eruptions were recorded between 1955 and 2009 (Okubo et al. 2009). In 2006, eruptions started to occur at a side vent, the Showa vent, adjacent to the summit Minamidake crater, on the south-eastern flank of the volcano (Yokoo and Ishihara 2007). Most eruptions now occur at the Showa vent, with only a very few (2-3 per year) occurring at the summit Minamidake crater (Smithsonian Institution 2009).

Typical, recent eruption sequences at Sakurajima begin with a phase of strombolian activity, when magma rises to the top of the conduit, and a weak, non-explosive eruption from an open vent causes ash and gas to be ejected intermittently (Yamanoi et al. 2008). As activity decreases, lava solidifies at the top of the conduit to form a vent cap (Yamanoi et al. 2008), sometimes also described as a dome (Ishihara 1985). Vulcanian explosions occur when the

solidified lava dome that caps the conduit ruptures, probably due to pressure from a gas pocket below the dome, leading to emissions of gas and ash (Ishihara 1985; Ishihara 1990).

The dispersal of eruption plumes from Sakurajima is a function of eruption type, magnitude, and wind velocity and direction (Kinoshita 1996). Plumes from Sakurajima vary from single, large eruption columns reaching several kilometres in height, to several, smaller eruption columns from numerous eruptions, to easily-diffused small plumes, with little or no ash (Durand et al. 2001). Horizontal plume patterns also vary greatly and, in conjunction with seasonal wind direction, a large range of dispersal patterns, which may change rapidly over time, can be observed at Sakurajima (Deguchi 1990; Kinoshita 1996).

Eto (2001) examined ash deposition and found that the amount of ash deposited (in g m^{-2}) and the average deposit grain size decreased with distance from the volcano, whilst the predominant direction of heavy ashfall varied seasonally. Kinoshita et al. (2000) also observed that under very strong wind conditions, plume collapse caused high total suspended particulate (TSP) and high SO_2 concentrations within 10 km of the volcano.

Review of health-related studies on Sakurajima ash

A total of 16 studies have been carried out on Sakurajima ash examining the effects on the respiratory system, summarised in Table 1.

Toxicological and clinical studies

Five toxicological studies have been carried out on ash from Sakurajima volcano. Shirakawa et al. (1984) and Samukawa et al. (2003) both concluded that the ash had some fibrogenic potential (ability to cause lung tissue scarring). Shirakawa et al. (1984) administered high

concentrations of ash (up to 50.4 mg m^{-3}) via intra-tracheal injection to rats and via inhalation to rats and rabbits (up to 500 mg ml^{-1}). They identified bronchitis, pulmonary emphysema, atelectasis lung, dust nodes and the onset of pneumoconiosis in their studies. Observations were conducted over long time periods (> 1 year) following instillation/inhalation to allow enough time for any delayed effects to be seen but they did not administer any positive or negative control dusts.

Samukawa et al. (2003) conducted a detailed investigation into the pulmonary effects of the ash and ash with SO_2 using an in vitro study on lung macrophages and in vivo investigations on rats. Ash was collected every day for a year, in order to administer representative samples. The in vivo study used a very high exposure (100 mg m^{-3}), but over a short time period (5 days). Particles were easily phagocytosed (engulfed by macrophage defence cells; the number and size of particles phagocytosed increased with time, up to 10 μm diameter) and no inflammatory response was measured. However, increased profilin mRNA was observed in vitro, which could indicate increased cell proliferation, and c-jun mRNA was expressed in the macrophages which may cause carcinogenesis, as has been seen in lungs exposed to asbestos. The authors expressed concerns that carcinogenic responses to volcanic ash exposure have not been studied at Sakurajima, especially as the most common cause of fatal cancer in males in Kagoshima has been lung cancer since 1980.

Kariya (1992) and Kariya et al. (1992) examined the lungs of deceased humans and dogs, respectively, who lived within a 10 km radius of Mount Sakurajima. In both cases, intrapulmonary particulate deposits and histopathological changes were examined and results were compared with control groups from low-exposure areas. In general, no statistically significant differences in any of the parameters were observed between exposed and control

groups in either study, although there was a higher incidence of squamous metaplasia in men and smokers in Kagoshima which could have been associated with a combination of smoking and SO_2 exposure. In Kariya et al. (1992) no indications of respiratory problems were observed in the lungs of any of the canines studied. However annual average Suspended Particulate Matter (SPM; equivalent of PM_{10}, thought by Yano et al. (1990) to be primarily from volcanic pollution) was higher in the 'control' towns than in Kagoshima, suggesting that more pollution in the control area may have affected the results.

Finally, Yano et al. (1985) studied the in vitro effects of ash on human lungs using serum. Their observations showed ash to be less toxic in the lungs than TiO_2, often used as an inert standard, with no release of lysosomal enzymes from human neutrophils nor inflammatory markers. However the authors did highlight that the time period for their experiments may have been too short for the effects of long-term exposures or slow-developing diseases to be observed.

Epidemiological studies

Eleven epidemiological studies have been carried out to examine respiratory disease and effects of volcanic emissions (summarised in Table 1). Wakisaka et al. (1983a) found that the mortality rate due to bronchitis and emphysema were much higher than in the standard population in areas of high ashfall, and that the crude mortality rate from respiratory ailments correlated positively with frequency of eruption in close proximity to the volcano. Wakisaka et al. (1985; 1984) also examined mortality statistics from respiratory ailments as a function of distance from Sakurajima and amount of volcanic ashfall respectively. Wakisaka et al. (1984) observed that death from respiratory diseases was higher in the study area than the standard population and that increased mortality correlated with periods following ashfall >

300 g m^{-2} $week^{-1}$. Wakisaka et al. (1985) found a consistency between distance from the volcano and respiratory mortality ratios.

Wakisaka et al. (1989) used data on national health insurance to compare respiratory health in districts in Tarumizu with different exposures to volcanic ash. They found that treatment for acute respiratory complaints was higher in the districts with highest ashfall and a few patients who were diagnosed with pneumoconiosis were inhabitants of high ashfall districts. However, no data on occupation and medical history were examined. Finally, two studies (Wakisaka et al. 1978; Wakisaka et al. 1983b) specifically examined the effects of volcanic ash on school children. Again, volcanic ashfall was found to correlate positively with prevalence of respiratory problems. On the other hand, Uda et al. (1999) compared children living on Sakurajima, in Kagoshima and in Tarumizu, with a control group unaffected by volcanic emissions. The study concluded that cases of asthma and related respiratory disease were not higher in the areas affected by ashfall from Sakurajima.

Wakisaka & Yanagihashi (1986) found that SO_2 concentrations above 0.2 ppm led to an increase in mortality the following week throughout the study period. In Japan, the ambient air quality limit for SO_2 is 0.04 ppm (24 hour average). Other volcanic pollutants were not measured directly and no relationship between the number of eruptions and mortality was observed.

Yano et al. (1990; 1986) examined the respiratory health of women between 30 and 59 years with no additional occupational exposure to volcanic ash and no history of respiratory problems. These criteria were used to represent a sub-section of the population at lowest risk from respiratory disease. Yano et al. (1986) examined three areas, representing low, medium

and high volcanic ash exposures. Only a slight trend in mild respiratory disease increasing with increasing TSP values was identified. However, this was not correlated with the amount of ashfall or SO_2 concentrations and the overall prevalence of respiratory problems in all areas was still low.

Yano et al. (1990) repeated the study, redesigned to eliminate some sources of possible error in the 1986 paper. Respiratory effects on women were only examined in two towns, Kanoya (25 km from Sakurajima), with no industrial activities and few major roads but with heavy ashfalls, and Tashiro, a similar control town (50 km from Sakurajima). No significant differences in respiratory diseases were observed between the two towns, despite SPM being twice as high in Kanoya. Yano et al. (1990) examined exposure patterns, finding that highest exposures to thoracic volcanic ash were at moderate distances from the volcano and concluding that the risk of chronic disease was low as, although the eruption was long-lived, the individual events were very short and only occurred in particular areas. Yano et al. (1987) specifically examined the respiratory health of loggers who are likely to have increased exposure through remobilised ash. However, no relationship between ash exposure and respiratory health was found.

As can be seen, there is little consensus among different studies examining the effects of the ash erupted from Sakurajima on respiratory health. Differences in sample locations and methodologies mean that results are generally not comparable. Furthermore, many of the studies do not represent realistic exposure patterns, using TSP, SPM or total ashfall as a proxy for volcanic ash pollution (e.g. Kariya 1992), disregarding the effects of high concentrations of SO_2 in very local populations (e.g. Wakisaka et al. 1984), or using

unrepresentative ash samples (e.g. Yano et al. 1990) or exposures in toxicological studies (e.g. Samukawa et al. 2003).

Mineralogical studies

A few of the toxicological and epidemiological studies included some analysis of the properties of the ash, with results on the amount of inhalable ash being very variable. Yano (1986) observed that 97 % of an airborne sample (collected by a high volume air sampler on one day, 8 km from the crater) was < 10 μm and Shirakawa et al. (1984) found that 99 %, by count, of ash particles sieved to < 53 μm were < 10 μm. However, Koizumi et al. (1988) concluded that most of the ash that they examined was too coarse to be respirable, and Horwell (2007) found that, by laser diffraction, a bulk ash sample had only 1.95 vol. % of particles < 10 μm and only 0.86 vol. % < 4 μm. Different methods of grain-size analysis mean these results are not directly comparable, but they do demonstrate a wide range in the amounts of observed respirable material. Currently no research has tried to reconcile these fundamentally different results, highlighting the need for a detailed analysis of the volcanic ash.

Most studies that have identified cristobalite have not been examining health hazards but conducting mineralogical research. For example, Oba et al. (1984; 1980) identified cristobalite in the X-ray diffraction (XRD) patterns of their Sakurajima volcanic ash samples, but did not quantify the amount. From older eruptive activity, Kawano and Tomita (2001a) observed 10 wt. % cristobalite in ash from 1914 and Shiraki and Tomita (1993) identified cristobalite XRD peaks and minor tridymite in ash layers above 1914 pumice deposits. They also studied much older layers, finding that cristobalite was absent in ash which fell after a pumice fall in 1470 but that there were ‘particularly large amounts’ in ash erupted before

4,900 yr. B.P. Increased amounts of tridymite were also reported in the older ash samples. Reports of cristobalite in ash from the most recent eruptive phase have ranged from negligible to 5 wt. % (Yano et al. 1985; Yano et al. 1990). It is not clear how accurate the above data are as, until recently, XRD quantification of cristobalite was hampered by the overlapping peaks of plagioclase feldspar and cristobalite. In addition to high-resolution instrumentation becoming available, Le Blond et al. (2009) developed a technique for quantifying single mineral phases in mixed dusts which overcame this issue, so more consistent assessments of cristobalite content are now possible.

In addition to the above, Kawano and Tomita (2001b) carried out TEM-EDS on Sakurajima ash from a 1990 eruption and observed weathered layers on the surfaces of volcanic glass, feldspar and hypersthene. Weathering may alter the respiratory toxicity of volcanic ash by coating reactive surfaces with more inert minerals. They did not observe any cristobalite in that sample. It should be noted that they believe that the alteration is the result of interaction of ash with near-neutral to weakly-acidic solutions encountered in the crater i.e. that their sample, collected during ashfall in Kagoshima, was derived from re-mobilised ash, originally deposited in a low-temperature part of the crater.

Methodology

Sample collection and preparation

Samples were sourced predominately from ash erupted from Sakurajima volcano during the most recent eruptive phase. Some samples were also collected from deposits from the largest historical eruptions of Sakurajima (1914 and 1471-6) to examine potential health hazards should Sakurajima return to its previous eruptive styles.

The recent samples were obtained from various archived sources (see Table 2), were all collected fresh at the time of eruption, and had been stored appropriately to prevent contamination or weathering.

The historical samples were taken from two stratigraphic sequences at Nagasakibana quarry on Sakurajima and from an exposed road cutting (Figure 1). At all sites, the face of the deposit was scraped away, revealing un-disturbed deposit for sampling, although we cannot discount the possibility that fine material could have been redistributed within the deposits by water percolation over time (see Discussion). The main quarry deposit consists of three pumice falls (erupted in 1471-1476, 1779-1786 and 1914) that sit on top of the Tenpyohoji lava flow from AD 764. Samples were collected from ashfall layers overlying a pumice fall from the 1470s eruptions, located in the lower part of the deposit. Samples SAK_1479_Qu_1-8 were taken from an ash sequence that was ~45 cm thick and consisted of three sub-sequences, each made up of three distinct, progressively-finer layers of ash (Figure 2). Samples derived from the 1914 eruption were taken from a second exposure in the quarry (sample SAK_1914_Qu_9) and the exposed road cutting located on another part of Sakurajima (sample SAK_1914_RdC_10).

As the volcano was not active during fieldwork, we could not collect fresh, deposited or airborne ash. Samples were sourced from archives and had generally been collected from ash deposited outside the institutions or from Sakurajima itself (see Figure 1), and it was difficult to find samples from a range of locations and distances around the volcano, particularly in Kagoshima city. No samples were available from Tarumizu city, although it is also regularly exposed to ashfall. All samples were collected within 12 km of the volcano, so ash dispersion over larger distances could not be examined.

Samples were oven dried for a minimum of 12 hours at 80 °C and sieved through 2 mm and 1 mm meshes to remove particles > 2 mm (not defined as volcanic ash) and to prevent particles close to 2 mm damaging equipment (the Malvern Mastersizer). Samples < 1 mm were analysed in all cases.

Analytical methods

The methods employed in this study have been described in detail in previous studies (Horwell 2007; Horwell et al. 2007; Le Blond et al. 2009; Le Blond et al. 2010) so are explained only briefly here.

X-ray fluorescence (PANalytical Axios Advanced XRF spectrometer, University of Leicester, UK) was used to determine the major elemental oxide composition of all of the ash samples. Grain-size analysis was carried out by laser diffraction (Malvern Mastersizer 2000 with Hydro MU, University of Cambridge, UK), again on all samples, with a refractive index of 1.63 and adsorption coefficient of 0.1 according to Horwell (2007). The results were converted to cumulative volume percentages and the health-pertinent percentages were estimated by interpolation of the binned data. In order to incorporate the 1-2 mm fraction of the ash, in coarse samples, the data were rescaled, using the fraction weights measured after sieving. X-ray diffraction with static position-sensitive detection (XRD-sPSD; Enraf-Nonius diffractometer with an Inel curved PSD, Natural History Museum, UK) was used, following the internal attenuation standard (IAS) method of Le Blond et al. (2009) to quantify crystalline silica phases in the ash. In this method, reproducible, near-random XRD patterns can be acquired quickly (10 minutes) and single phases quantified (with < 3 wt. % error)

without prior knowledge of sample mineralogy. This technique was carried out on 13 samples, selected for their fineness and to reflect different eruption dates and conditions.

Further analyses were carried out on a sub-set of seven samples, chosen for their pristine condition in addition to the above parameters. Scanning Electron Microscopy (Hitachi SU70 FEG-SEM, Durham University, UK, with 8 kV and ~10.5 mm WD) was used to obtain information on particle morphology. Particles were deposited on to carbon sticky tabs on Al stubs and coated with 20 nm Pt. In addition, specific samples were studied in further detail (based on high cristobalite content and fine grain-size distribution) by Transmission Electron Microscopy (Jeol 2100F FEG-TEM, Durham University, UK, 200 kV) for the potential identification of cristobalite nano-fibres. Particles, suspended in isopropanol, were deposited onto copper TEM grids coated with holey carbon.

Specific surface area (SSA) was measured using the Branauer Emmet Teller (BET) method (Micromeritics TriStar 3000 Surface Area and Porosimetry Analyser, Durham University, UK) with nitrogen gas. Samples were outgassed at 150 °C overnight and analyses repeated twice.

Fubini et al. (1995) used electron paramagnetic resonance (EPR) with spin-trap as a direct measurement of free radicals produced by fractured surfaces in order to estimate the surface reactivity of particles in mineral dusts. Here we tested the ability of the ash to generate the hydroxyl radical through replication of the Fenton reaction (Eq.1) following the method of Horwell et al. (2007) where iron from the ash reacts with hydrogen peroxide to generate the radical. The experiments were carried out for 60 minutes. At 10, 30 and 60 minutes a sub-sample of each solution was analysed in the EPR spectrometer (Miniscope 100 ESR

spectrometer, Magnettech, Università degli Studi di Torino, Italy). Mn^{2+} in $CaCO_3$ was used as a calibration standard, which was incorporated into the final calculations. Two repeats were carried out for each sample. Results were averaged and expressed per unit area of ash using the results from BET analyses.

Quantifying the amount of iron available at the surfaces of ash particles is important due to the role of surface Fe^{2+} in the Fenton reaction. Spectrophotometry (Uvikon UV-vis spectrophotometer, Università degli Studi di Torino) was used to determine the amount of iron that could be released from the ash surface in the lungs. Ferrozine chelator (specific to Fe^{2+}) was used to remove iron from the particle surface. Samples were analysed in the absence and presence of the reductant ascorbic acid to quantify the Fe^{2+} and total Fe present following a method previously described (Horwell et al. 2007). Measurements were taken at 4 hours, 24 hours and once every 24 hours over 7 days, except for the weekend.

For surface reactivity and iron release, the Sakurajima samples were analysed alongside Min-U-Sil 5 quartz standard (U.S. Silica, Berkeley Spring plant, SSA = 5.2 $m^2\ g^{-1}$), ash from the Soufrière Hills volcano (SHV), Montserrat (MBA5/6/99, SSA = 1.28 $m^2\ g^{-1}$) and Mt. Etna (Italy, SSA = 0.19 $m^2\ g^{-1}$) (Horwell et al. 2007). Min-U-Sil 5 was chosen because it is a quartz of well known toxicity and surface reactivity (Elias et al. 2000; International Agency for Research on Cancer 1997), is widely employed for in vitro and in vivo experimental studies on silicosis, and has been consistently used as a standard in volcanic ash EPR studies (Horwell et al. 2007; Horwell et al. 2003a; Horwell et al. 2010b; Le Blond et al. 2010). Soufrière Hills ash was chosen because it has been extensively characterised mineralogically (Horwell et al. 2003b) and toxicologically (Lee and Richards 2004; Wilson et al. 2000), and MBA5/6/99 has consistently been used as a comparison andesitic sample in several studies

(Horwell et al. 2007; Horwell et al. 2010b; Le Blond et al. 2010). The basaltic, iron-rich Etna sample was chosen because is extremely reactive in free radical generation (Horwell et al. 2007) and has also been used as a standard sample in other studies (Le Blond et al. 2010).

The human erythrocyte lysis assay (haemolysis) was used to examine the potential for ash particles to cause silica-like rupture of red blood cell membranes (Clouter et al. 2001) for three samples (chosen for their high cristobalite content and fine grain-size distribution). This basic assay is used as a first indicator of potential toxicity of mineral particles. Erythrocytes were obtained from fresh human venous blood and washed with sterile saline. Analyses were carried out three times using a range of particle doses (0.06 - 2.0 mg ml^{-1}) with 30 min. incubation (Centre for Inflammation Research, University of Edinburgh, UK). Positive (DQ12 quartz) and negative (ultrafine TiO_2) controls were also included.

Results

Major element ash compositions from XRF are plotted on a total alkali vs. silica plot (TAS) in Figure 3. Almost all the samples from recent activity (5^{th} phase) are andesitic apart from two samples which sit just inside the basaltic andesite category. The historical samples show a compositional change, as those collected at the quarry from the 1470s eruptions (Bunmei era) are dacitic, whilst the samples from the 1914 (Taisho era) deposits are andesitic. Within the andesitic envelope of samples collected during recent activity, no temporal trend in magmatic composition is observed.

A wide range in the proportions of respirable (< 4 μm) and thoracic (< 10 μm) material among samples is evident from the grain-size results (Table 3). The volcano has the potential to produce large proportions of very fine ash (up to 18.8 vol. % < 4 μm material in the

historical samples and up to 9.7 vol. % in the recent samples), but many samples are also very coarse-grained. Factors which could govern spatial grain-size distribution patterns were not examined in detail in this study due to the highly-localised and rapidly-changing nature of eruptions at Sakurajima, the limited range of variables (e.g. distance/direction from the volcano) represented in the samples available and inadequately-detailed information about eruptions recorded at the time of collection for some samples.

Cristobalite was present in all of the samples analysed, however no quartz or tridymite were identified. The weight percentages of cristobalite in the samples are low, ranging between 1.4 - 5.7 wt. % with < 3 wt. % error (Table 4). The historical samples from the 1470s ashfall layers have low cristobalite contents (1.4 and 2.1 wt. %), the sample from the 1914 eruption has slightly higher content (~ 4.3 wt. %), and the amount of cristobalite in the recent samples analysed is 2.8 - 5.7 wt. %. Samples SAK_2008_AMU_31 and SAK_2008_FUR_32, which had the lowest and highest cristobalite contents, respectively, out of the recent samples, were erupted within a few days of each other. The first (lowest) sample was collected after the first reported eruption for over a month, however no ash was observed in satellite data. The highest sample, collected 3 days later, was collected during several days of explosions and ash venting.

The morphology of the particles examined from Sakurajima is quite variable. Some particles are typical non-vesicular blocky ash particles, some are clearly glass with conchoidal fractures, and others are unusually porous ‘particles’ that may be single crystals/rock fragments or welded aggregates (Figure 4). Many respirable grains could be identified, especially adhered to the surface of larger particles. A few fibre-like particles were observed, however, they were not related to asbestos in composition (by EDS) nor morphology and

were too sparse to be a potential respiratory health hazard. Fibre-like particles were examined in further detail by TEM. We observed sparse, nano-scale fibres but, again, none were related to asbestos nor crystalline silica, instead being sulphates and Al-rich alumino-silicates.

The specific surface area for the Sakurajima samples varies between 0.5 - 3.8 $m^2 g^{-1}$ (Table 4), which sits within the range of previously-published data for volcanic ash (0.2 – 6.9 $m^2 g^{-1}$ (Horwell et al. 2007; Horwell et al. 2010b; Le Blond et al. 2010)). The number of hydroxyl radicals generated per unit surface area for the samples was at the lower end of the spectrum of previously-published data (Horwell et al. 2007; Horwell et al. 2003a; Horwell et al. 2010b; Le Blond et al. 2010) (Figure 5), sitting in the area expected for andesitic samples, such as the Soufrière Hills standard sample. In agreement with previously published work, the basaltic Etna standard sample generated far more radicals than the more silicic samples (3.2 μmol m^{-2}). All of the Sakurajima samples produced values between 0.09 and 0.22 μmol m^{-2} at 30 minutes incubation except two samples which generated 0.57 and 1.35 μmol m^{-2} of hydroxyl radicals (samples SAK_2000_Kag_30 and SAK_1985_Ara_21, respectively). Distinctions between these samples are difficult to make as such low results mean that the differences between the samples are extremely small and often the results lie within the analytical uncertainties.

Horwell et al. (2007) highlighted that the ability of surface iron to produce radicals is influenced by the state of the iron at the surface. For example, Fe_2O_3 and Fe_3O_4 have been shown to be 'inactive' and excess surface iron may reduce reactivity (Fubini et al. 1995). The iron release experiment was designed using chelators that extracted poorly co-ordinated surface iron ions that would be more likely to be available to react in the lungs (Horwell et

al. 2007). The amount of total iron (both in the reduced and oxidized forms) available at the surface of ash particles is comparable for most samples, ranging between 25 and 45 μmol m^{-2} at 7 days of incubation, as is also seen with the Soufrière Hills sample. There is little correlation between hydroxyl radical generation and iron release when iron release is low (Figure 5), as was observed by Horwell et al. (2007). However, sample SAK_1985_Ara_21 released more iron (70 μmol m^{-2}) and commensurately generated more radicals, setting it apart from the other samples but not enough to place it amongst the more basaltic samples analysed by Horwell et al. (2007) or the Etna sample re-analysed here. However, the results for total iron release and hydroxyl radical generation in this study do seem to indicate that, above a certain threshold of iron release, higher amounts of total iron available at the surface lead to increased hydroxyl radical generation. No apparent trends between hydroxyl radical generation and Fe^{2+} release were evident (data not shown for brevity). However, even trace amounts of Fe^{2+} may trigger the catalytic Fenton reaction and, in the body, Fe^{3+} may also generate hydroxyl radicals, indirectly, if reducing agents such as ascorbic acid, cysteine or glutathione are present (Fong et al. 1976; Halliwell and Gutteridge 1984; Park and Imlay 2003 ; Zager and Burkhart 1998).

All Sakurajima samples produced more radicals than the Min-U-Sil 5 quartz toxic standard, and also released more iron ions. These results are consistent with data obtained from all previous volcanic ash samples analysed (Horwell et al. 2007; Horwell et al. 2003a; Horwell et al. 2010b; Le Blond et al. 2010).

The erythrocyte lysis assay showed a low propensity for haemolysis, although two out of three samples (SAK_2008_N_38 and SAK_2000_Har_27) showed mild haemolytic potential

(3.3 and 5.5 % haemolysis at 2 mg ml^{-1} respectively compared with 0.7 % for TiO_2 and 31.9 % for DQ12 quartz).

Discussion

The results of this study show that the Sakurajima ash varies considerably in its composition and grain-size distribution. This is unsurprising considering the range of eruption types, magnitudes and plume dynamics at the volcano, but it makes assessment of the health hazard, based on physical and bulk compositional parameters, challenging and generalisations for the volcano are not possible.

The trends in bulk composition are in keeping with other studies that have demonstrated a decrease in SiO_2 content with time for each of the major historical eruptions of Sakurajima volcano (Uto et al. 2005; Yanagi et al. 1991), and a lack of clear trend in recent eruptions, as noted by Ishihara (1999).

The amount of respirable material resulting from the vulcanian eruptions at Sakurajima is in keeping with observations at other andesitic vulcanian eruptions where samples have been collected < 10 km from the vent, e.g. Soufrière Hills volcano, Montserrat, in September-October 1997 (Horwell 2007; Horwell et al. 2003b). However, the proportion of respirable material in some samples is greater than expected considering the proximity of samples to the crater and the comparatively small size of eruptions. This could be because of a high degree of fragmentation from the explosive destruction of the lava plug/dome that seals the conduit before an eruption.

The few, extremely fine-grained layers in the 1470s plinian deposit (nos. 3, 6, 8 on Figure 2), containing up to 18.8 vol. % < 4 μm material, appear to demonstrate the potential for the volcano to produce considerable quantities of respirable ash during larger, plinian-style eruptions. This amount of respirable material has only previously been documented during phreatomagmatic eruptions of Vesuvius, Italy (~ 17 vol. % < 4 μm material) (Horwell et al. 2010b). Given that these samples were obtained from ancient deposits, we must also consider the possibility that the samples are affected by re-distribution of fines by percolation of water through the deposits. It has been shown that the ratio of < 10 to < 4 μm particulate in any given ash sample is usually close to 2:1 (Horwell 2007; Horwell et al. 2010b) (R^2 = > 0.98). To test whether the historical ash samples in this study are affected by re-distribution of material, we have plotted the abundance of < 4 μm ash against < 10 μm ash from this study (Figure 6) and find that the historical samples (1470s and 1914) appear to plot on a separate trend from the fresh ash samples (which are close to the expected 2:1 ratio). The historical samples are slightly depleted in < 4 μm ash, indicating that the sample size distribution has been modified by the loss of up to 4 vol. % < 4 μm material (for the sample with the most abundant < 10 μm material). As the historical samples actually contain up to 30 vol. % more < 10 μm ash than the fresh samples, it is clear that, despite any loss of < 4 μm material, some of the historical samples still contain significantly more fine ash than the fresh samples; we can, therefore, attribute this to the enhanced explosivity of the plinian eruptions which generated the ash. Although the volcano may not return to a period of plinian activity in the near future, individuals may still be exposed to the ash through quarrying of deposits if appropriate measures to limit fine particulate exposure are not being taken.

Samples from the most recent eruptive phase contained a wide range of respirable material (1.1 – 9.6 vol. % < 4 μm). Previous studies have found the ash produced by Sakurajima to be very coarse-grained, with little health-relevant material (Horwell 2007; Koizumi et al. 1988; Yano et al. 1990), whilst others observed larger proportions of fine material (Oba et al. 1984; Shirakawa et al. 1984; Toyama et al. 1980; Yano 1986). The range in results seen here therefore accounts for disparities within the literature, which appear to be caused by the natural variability of ash produced by the volcano in addition to different analysis techniques and distances of ash collection. Whilst this study does show that proximal Sakurajima ash can be fine, we were unable to consider distal samples in this study and therefore recommend that further work is done which addresses the exposure of populations > 10 km from the volcano.

The large variability reflected in the grain-size results was not observed in the crystalline silica content of the samples, which remained relatively constant (< 6 wt. %) over a range of eruption dates and styles. All of the crystalline silica observed was identified as cristobalite, in contrast to some previous work (Shiraki and Tomita 1993). At other dome-forming volcanoes, cristobalite content in dome-collapse ash (also known as co-ignimbrite ashfall) may be expected to be between 10 - 20 wt. % of bulk ash (e.g. at Soufrière Hills volcano, Montserrat and Chaitén volcano, Chile: Horwell et al. 2010a). During explosive eruptions, where no dome is present, cristobalite contents are usually negligible, e.g. ~ 1 - 3 wt. % at Rabaul, Papua New Guinea (Le Blond et al. 2010), although Reich et al. (2009) did observe cristobalite nano-fibres in Chaitén ash from the early, explosive phase of the 1998 eruption. Here we see the greatest amounts of cristobalite in the recent vulcanian eruptions (~3 - 6 wt. %), indicating that some cristobalite is formed in the small dome prior to destruction by the explosion, or that cristobalite-containing edifice rock is incorporated during the explosion.

We confirmed by TEM that the cristobalite was not formed in the explosion column as cristobalite nano-fibres. Within the dome, cristobalite is likely to have formed by vapour-phase deposition in vugs or by devitrification of volcanic glass as described for other volcanoes (Baxter et al. 1999; Horwell et al. Submitted). Studies at Chaitén volcano have demonstrated that cristobalite can be formed rapidly in the dome environment, with large amounts of cristobalite being formed within 3 months, probably by vapour-phase crystallisation (Horwell et al. 2010a), and work at the Soufrière Hills volcano demonstrated that cristobalite can form within hours to days of a magma packet being injected into the dome (Williamson et al. 2010). Therefore small amounts of cristobalite could be formed at Sakurajima, even when dome growth is short-lived.

The lowest cristobalite values are observed in the plinian deposits, which is expected as cristobalite is generally not found in large magmatic eruptions unless there is entrainment of edifice/upper conduit material or an existing dome, which would anyway constitute a small proportion of the total erupted material (Horwell et al. 2010b).

In occupational settings, the effects of mineral dust exposures are well-studied, but workers are likely exposed to higher quantities of dust and for longer durations than populations exposed to volcanic ash. Nevertheless, occupational studies can help to estimate potential threats from Sakurajima ash. Chronic diseases generally only occur after years of exposure on an almost daily basis and with high concentrations of respirable crystalline silica (AIOH 2009), although short-term, very-high exposures may be more hazardous than equivalent exposures at lower levels over longer timescales (Buchanan et al. 2003). Some recent studies have highlighted that risk from crystalline silica may have been underestimated, with

reported cases of silicosis in people working within legal exposure limits (Park et al. 2002). Despite this, the low amounts of cristobalite in the Sakurajima ash samples, the fact that the silica will be inhaled along with aluminosilicate and glass, potentially diluting its effects, and the generally lower toxicity of ash samples in toxicological tests compared to positive controls such as DQ12 quartz (Koizumi et al. 1988; Yano et al. 1985) indicate that the potential for the development of chronic, silica-related respiratory disease from Sakurajima ash inhalation is low.

However, the extended duration of exposure to ash in the populated areas around the volcano means that disease caused by frequent exposure to low-levels of crystalline silica or volcanic ash in general cannot be totally ruled out, and a dedicated exposure risk assessment such as that done at Soufrière Hills volcano (Cowie et al. 2003; Hincks et al. 2006) would be valuable. Japan has 24h and annual environmental air quality standards for TSP and $PM_{2.5}$ (http://www.env.go.jp/en/air/aq/aq.html) so it would be useful to know whether these standards are exceeded regularly during and after specific eruptions, however these data were not available for this study. We have also not considered the interaction of the ash with volcanic SO_2 or with anthropogenic aerosols and the potential cumulative effect that such exposure could have on human and animal health.

In addition, it was beyond the scope of this study to determine the effects of inhaling re-suspended ash. Following eruption, it is unclear whether the grain-size distribution of deposited ash changes significantly over time, from pulverization or disaggregation of chemically-bonded particles by vehicles, human disturbance or aeolian action. However, available evidence from Soufrière Hills volcano suggests that ash surface area is increased by grinding, hence grain-size decreases (Horwell et al. 2003a) and that concentration of ash re-suspended by vehicles decreases exponentially with height, indicating higher exposure for

children compared with adults (Horwell et al. 2003b). We recommend that studies involving re-suspension and interaction with other aerosols are carried out in addition to formal risk assessments and exposure studies.

Examination of surface reactivity in the ash samples found the production of hydroxyl radicals to be low in comparison to more iron-rich ash samples and, for the most part, samples were also less reactive than the Soufrière Hills andesitic ash. This is consistent with Horwell et al. (2007; 2003a; 2010b) who found that hydroxyl radical release correlated with surface iron availability, with andesitic ash samples tending to have much lower surface reactivity than basaltic samples. It is also possible that the ash surfaces had been altered, if some fraction of the samples were derived from re-mobilised ash from the crater, as observed by Kawano and Tomita (2001b).

A sustained inflammation, upon oxidative damage, may play a key role in the adverse effects elicited by inhaled dusts. Oxidative damage may be due to both generation of radical species (particle-derived and cell-derived free radicals) and depletion of antioxidant defences. It is assumed that the most abundant in vivo production of hydroxyl radicals according to the Fenton reaction occurs in presence of iron and copper. However, the Fenton reaction may also occur in presence of other transition metals such as As(V), Be(II), Cd(II), Co(II), Cu(II), Hg(II), Pb(II), and Ni(II) (Jomova and Valko 2011; Stohs and Bagchi 1995) some of which occur as trace elements in volcanic ash. It is not clear whether manganese, which is sometimes leached from ash in greater quantities than iron into lung fluid stimulants (G. Plumlee, pers. comm.), has the ability to alter the kinetics of cellular free radical production, with different studies giving conflicting results (Ali et al. 1995; Donaldson et al. 1982; Hussain and Ali 1999; Shi and Dalal 1990).

All samples were more reactive than the Min-U-Sil 5 quartz toxic standard. This is explained by the fact that, in addition to the ability to release free radicals in solution, several other physicochemical characteristics play a significant role in quartz toxicity, particularly when considering particle surface-cell interactions. These include, but are not limited to: (i) the extent of surface silanols and surface charges, (ii) the presence of surface silica radicals, (iii) crystal structure and particle micro-morphology (Fenoglio et al. 2000; Fubini 1998; Warheit et al. 2007). To date, however, any attempt to relate one single physicochemical property to the pathogenic response has been unsuccessful, probably because several surface properties are implicated and various particle/living-matter interactions take place.

The ambiguity of the toxicology studies for Sakurajima ash does emphasize the need to examine potential sources of toxicity (e.g. transition metal-catalysed radical generation) other than crystalline silica, but the low release of hydroxyl radicals and the low haemolysis seen in these experiments indicate that the potential of the samples to cause respiratory disease via these mechanisms is likely to be low.

Conclusion

The potential respiratory hazard from Sakurajima ash was examined from a mineralogical, geochemical and toxicological perspective. The grain-size distributions were variable due to a combination of different eruption mechanisms, explosivity and, in all likelihood, plume dynamics, but the data resolve the main issue, that Sakurajima does have the potential to produce considerable amounts of respirable material, especially during major plinian eruptions. With the current style of vulcanian eruptions, however, the amount of respirable ash produced is relatively low (never above 10 vol. % < 4 μm material). This result needs to

be considered alongside the long timescales for potential exposure of local populations, and further investigation of exposure patterns is warranted to better constrain the risk of ash causing disease. The characteristics of the volcanic ash should also continue to be monitored to help give current and relevant advice to the exposed populations as eruption conditions change.

Cristobalite was identified in all samples, and was the only crystalline silica polymorph observed. Fairly low quantities are produced, suggesting that high, and long-lasting, exposure to ash would be needed to develop silica-related disease. Hydroxyl radical release from the samples was low compared to other volcanic samples, indicating that iron-related reactivity, as a mechanism for disease, is unlikely at Sakurajima volcano.

In the absence of further studies, however, precautions should be taken to reduce ash exposure, especially in occupational settings such as quarrying of the plinian deposits, but also for those clearing ash from new ashfall events.

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Figure Captions

Figure 1. a) location map of Sakurajima volcano. b) locations of samples analyzed in this study (circles). Sample location abbreviations (see also Table 2):

Qu	Nagasakibana Quarry
RdC	Road Cutting (1914 deposit)
SVO	Sakurajima Volcano Observatory (now known as the Sakurajima Volcano Research Center)
FUR	Furusato Museum
Kur	Kurokami Observation Station
Uto	Utoko fishing village
Shr	Shirahama town
Har	Old SVO/SVRC building – Haratuyama Branch
Kag 28	Arena area, Kagoshima
Kag 29	Tsurumaru area, Kagoshima
Kag 30	Residential house in Kagoshima
SBT	SBT Observation Point
AMU	Arimura Lava Observatory
EHS	East Sakurajima School
Ara	Arata, previously JMA offices
HRT	Haratuyama Seismic Tunnel
KOP	Kom Observation Point
DoP	Dolphin Port, Kagoshima

Figure 2. Sequence of ash layers located above the 1470 pumice fall at Nagasakibana Quarry (Qu in Fig. 1). Grain-size abbreviations: **P**: pumice (dots and ovals); **C**: coarse-grained ash (dots); **F**: fine-grained ash (diagonal lines); **VF**: very fine-grained ash (blank). Numbers indicate sample locations (sample numbers prefaced with SAK_1479_Qu_; see Table 2 for details).

Figure 3. Total alkali-silica plot for all samples analysed.

Figure 4: Scanning electron microscopy images of a: SAK_1479_Qu_8 showing particularly fine-grained samples, and b: SAK_2000_Har_27 showing typical particles < 10 μm.

Figure 5. The amount of hydroxyl radicals released at 30 minutes after the start of the experiment compared to the total iron released after 7 days. Min-U-Sil quartz values published in Horwell (2007). Hydroxyl radical generation data for MBA5/6/99 (from Soufrière Hills volcano, SHV) and ETNA collected with current samples but Fe release values measured in July 2008, published in Le Blond et al. (2010). SAK_2008_N_38 sits immediately under SAK_2008_FUR_32.

Figure 6. Correlation plots of health-pertinent size fractions for fresh and historical ash samples.

Table 1. Summary of studies considering respiratory health from inhalation of volcanic ash from Sakurajima volcano.

Reference	Study Type	Study Description	Key Observations	Comments
Samukawa et al., 2003	Toxicological	In vivo studies with ash (4.3 µm mass median aerodynamic diameter) and SO_2 in rats. Inhalation exposure 100 mg m^{-3} ± 1.5ppm SO_2, 4 h/day for 5 days followed by lavage.	80 % of macrophages had phagocytosed ash after 1h. Profilin mRNA content of macrophages elevated and c-jun mRNA expressed. Results indicate some inflammatory and fibrogenic potential.	Very high exposures used. Ash collected daily during 1993, wet ash excluded.
Yano et al., 1985	Toxicological (some mineralogy)	Characterisation of one ash sample and in vitro experiments with V79-4 cells and human serum.	The effects of the ash were similar to an inert control. Negligible cristobalite content.	Experiments may have been too short to observe developments of long-term respiratory disease.
Shirakawa et al., 1984	Toxicological (some mineralogy)	Ash characterisation (bulk elemental and mineral composition, grain-size). In vivo studies on rats and rabbits. Inhalation: up to 50.4 mg m^{-3} of '< 270 mesh' administered 4 h/day for 112 days with longest survival 961 days. Instillation: up to 500 mg ml^{-1} saline of '< 325 mesh' ash with longest survival 354 days.	93% ash particles < 55 µm were thoracic. Bronchitis, onset of pneumoconiosis and dust node shadows observed.	Long time periods allowed time for development of symptoms. Very high dosage used.
Kariya, 1992;	Toxicological	Intrapulmonary particulate deposits (IPD) and histopathological changes studied in human lungs.	No significant differences attributable to ash exposure were observed between the two groups.	Annual average SPM* higher in 'control' city compared to Kagoshima.
Kariya et al., 1992	Toxicological	Examined lungs of stray dogs for IPD and histopathology.	No differences observed between exposed and control group.	Annual average SPM* higher in 'control' city. Did not use thoracic content for ash exposure values.
Uda et al., 1999	Epidemiological	Comparison of asthma cases in children affected by ash and a control group using questionnaires.	No differences observed between exposed and control group.	
Yano et al., 1990	Epidemiological (& exposure patterns)	Respiratory health of women in exposed and control populations examined by questionnaires. SPM measurements also taken.	Highest SPM mid-distance (20-40 km) from the volcano yet no significant differences between the areas were observed.	
Wakisaka et al., 1989	Epidemiological	Examined national health insurance claims in districts of Tarumizu with varying amounts of ashfall.	Higher number of treatments for acute respiratory problems in high ashfall districts.	

Yano et al.,1987	Epidemiological	Respiratory health of loggers exposed to remobilised ash.	No evidence to show ash exposure adversely affected respiratory health.	
Yano et al., 1986	Epidemiological (some mineralogy)	Respiratory health of women examined by questionnaire from areas with different exposures. Studied grain-size of airborne sample.	A slight increase in mild respiratory symptoms with increasing TSP values. Airborne sample with 97 % < 10 µm.	Inaccuracies in estimation of exposure patterns (see Yano et al., 1990).
Wakisaka & Yanagihashi 1986	Epidemiological	Week to week mortality investigated compared to volcanic pollution.	Seasonal trends observed and increased mortality following SO_2 > 0.2 ppm.	Trends not directly attributable to ash.
Wakisaka et al., 1983a	Epidemiological	Examined mortality statistics for respiratory ailments in Kagoshima.	Identified spatial trends in mortality that could be associated with volcanic pollution.	Volcanic pollution definition did not consider thoracic content.
Wakisaka et al., 1984	Epidemiological	Studied mortality statistics in Kagoshima and Tarumizu for particular respiratory diseases.	Correlations identified between volcanic ash and increased mortality from respiratory illnesses.	Exposure to volcanic ash based on annual ashfall figures. Thoracic content not considered.
Wakisaka et al., 1985.	Epidemiological	Examined mortality statistics (1968-1982) for respiratory ailments within 50km of Sakurajima.	Correlation between distance from the volcano and respiratory mortality, which peaked in 1974 with volcanic activity.	Studies only conducted within 50km of the volcano, correlations not based on exposure.
Wakisaka et al., 1978, 1983b	Epidemiological	Examined the effects of volcanic ash on the respiratory health of school children in Kagoshima prefecture.	Found a positive correlation between volcanic ash exposure and decreased respiratory health in school children.	Studies conducted in local areas only.
Horwell, 2007	Mineralogical	Grain-size analysis using laser diffraction of samples from many volcanoes including Sakurajima.	Ash was very coarse with little thoracic or respirable material.	Only one sample examined.
Yano, 1986	Literature summary	Summarised several of the latter studies as well as the author's own data.	Further work recommended as even a negligible risk could not be neglected with such large populations and timescales.	
Koizumi et al., 1988	Literature summary	Scrutinized a number of the latter studies.	Concluded that the ash was too coarse to become a chronic hazard.	

*Suspended Particulate Matter (equivalent to PM_{10})

Table 2. Sample summary. Samples grouped where collected from identical location and listed chronologically.

Sample I.D.	Eruption date	Eruptive Era	Location	Archive source	Notes
SAK_1479_Qu_1 – 8	1471 – 1479[1]	1 – Bunmei phase	Nagasakibana Quarry		
SAK_1914_Qu_9/RdC_10	1914[1]	3 – Taisho phase	Nagasakibana Quarry/Road cutting		
SAK_1958_EHS_11	09.06.1958	5 – current phase	E. Sakurajima High School	JMA[2]	
SAK_1974_Har_12	15/16.12.1974	5 – current phase	SVRC, Haratuyama Branch	SVRC[3]	2 small explosions
SAK_1979_Ara_13	14/15.10.1979	5 – current phase	Arata, Kagoshima	JMA	Collected after a series of explosions/ash emission, during a particularly active 3 month period.
SAK_1981_Ara_14	08/09.06.1981	5 – current phase	Arata, Kagoshima	JMA	
SAK_1983_Ara_15-16	17.09 – 30.11.1983	5 – current phase	Arata, Kagoshima	JMA	During a period of frequent explosive eruptions. Large eruptions noted before collection. Precipitation noted.
SAK_1984_Ara/SVO_17-20	06.05 – 25.07.1984	5 – current phase	Arata (Kagoshima)/SVRC	JMA/SVRC	Collected during intermittent periods of intense activity (2-5 eruptions per day lasting 2-7 days)
SAK_1985_Ara_21	25/26.08.1985	5 – current phase	Arata, Kagoshima	JMA	Collected after one large eruption during a period of decreasing explosions.
SAK_1987_Ara_22	13/14.10.1987	5 – current phase	Arata, Kagoshima	JMA	Very small amount of ash deposited in Kagoshima, no eruption noted.
SAK_1988_Ara_23	15/16.06.1988	5 – current phase	Arata, Kagoshima	JMA	Largest recorded ashfall (2671 g m^{-2}) since 1969 after 2 large eruptions
SAK_1990_Ara_24	10/11.04.1990	5 – current phase	Arata, Kagoshima	JMA	Small ashfall. Precipitation.
SAK_1992_Ara_25	27/28.06.1992	5 – current phase	Arata, Kagoshima	JMA	Small ashfall, no explosion. Precipitation.
SAK_1997_FUR_26	03.12.1997	5 – current phase	Furusato Museum	SVRC	70,000 tons ash erupted after a single, large eruption. Collected during the first few hours of the eruption. Ash cloud extended

					25-50km south and east.
SAK_2000_Har_27	06.06.2000	5 – current phase	SVRC, Haratuyama Branch	SVRC	
SAK_2000_Kag_28-30	07.10.2000	5 – current phase	Kagoshima. See [4] for detail.	SVRC	Collected during large eruption.
SAK_2008_FUR/AMU_31-33	3-6.02.2008	5 – current phase	Furusato/Arimura	Furusato Museum[5]	1st eruption for a month, beginning with ash venting and continuing for several days of ash venting and explosions.
SAK_2008_FUR_34-35	11-14.04.2008	5 – current phase	Furusato Museum	Furusato Museum[5]	Ash collected on 3rd day of small eruption during quiet period.
SAK_2008_FUR_36	22.04.2008	5 – current phase	Furusato Museum	Furusato Museum[5]	Collected after explosions on the 1st day of a 5 day eruption sequence of ash venting and explosions.
SAK_2008_N_37-41	7-9.05.2008	5 – current phase	Various locations around volcano. See [6] for detail.	SVRC	Samples collected from various points around Sakurajima volcano after 2 eruptions with persistent ash in the atmosphere.
SAK_2008_FUR_42-43	20-21.05.2008	5 – current phase	Furusato Museum	Furusato Museum	Collected on the 7th/8th days of intense activity (~1-2 explosions) per day. Precipitation.
SAK_2009_N_44-51	20-22.08.2009	5 – current phase	Various locations. See [7] for detail.	SVRC	Collected during an explosion and over subsequent days of ash venting and small explosions.

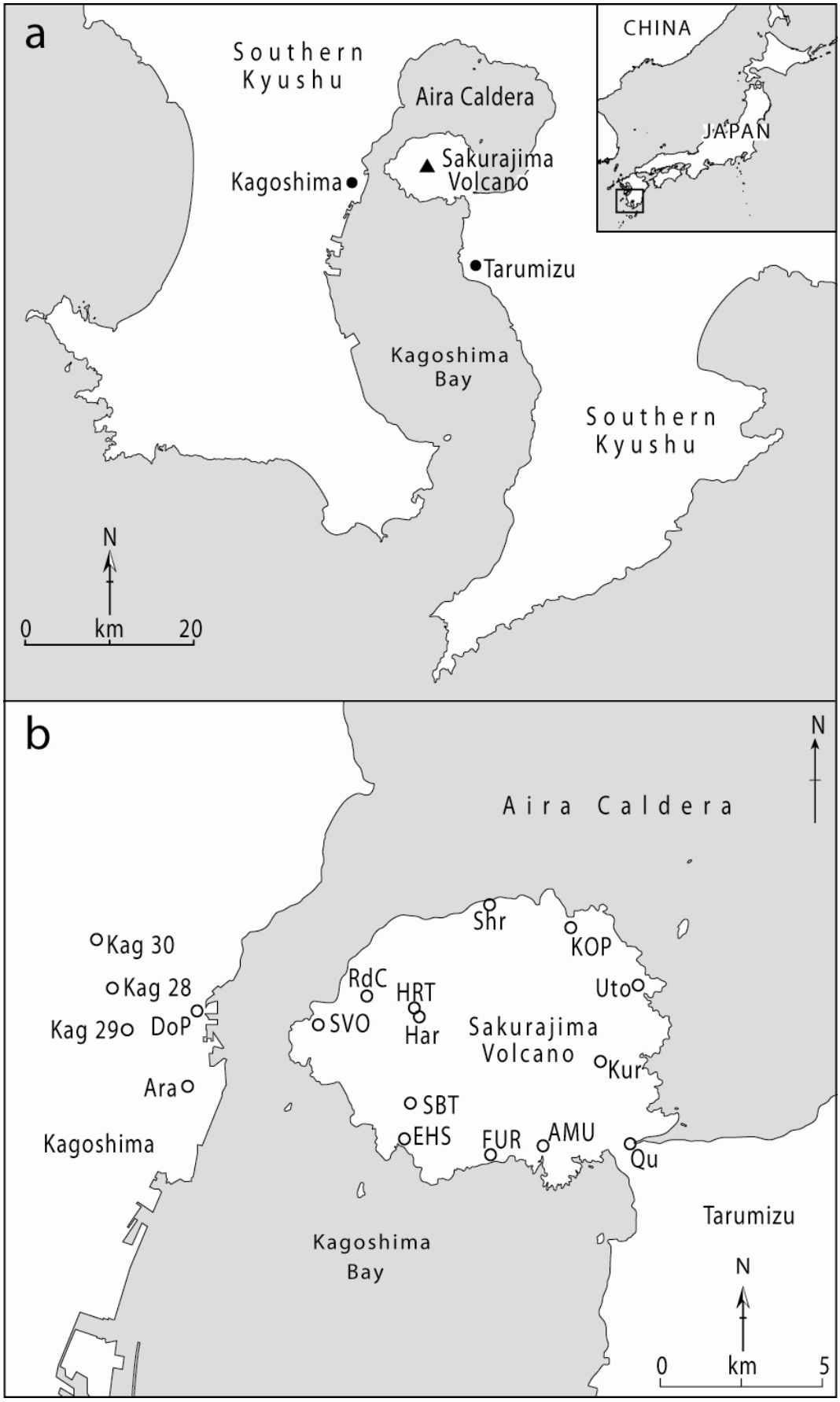
[1] Samples collected on 11.11.2008
[2] JMA is the Kagoshima branch of the Japan Meteorological Agency.
[3] SVRC is the Sakurajima Volcano Research Center, DPRI, Kyoto University (previously known as the Sakurajima Volcano Observatory, SVO).
[4] Sample locations are: Arena (28), Tsurumaru (29) and 'site 3' (30) all in Kagoshima.
[5] Samples collected from a concrete surface outside of Furusato Museum.
[6] Sample locations are: SVRC (37), Furusato (38), Kurokami (39), Utoko (40) and Shirahama (41)
[7] Sample locations are: Haratuyama Tunnel (44, 50), Kurokami (45), Kom. Observation point (46), SVRC Haratuyama Branch (47), SVRC (48), Kurokami (49) and Dolphin Port, Kagoshima (51). NB. SAK_2009_N_46 not analysed as sample too small.

Table 3. Proportion of respirable and thoracic material in all samples sorted by quantity of < 4 µm material (volume %).

Sample I.D	< 4 µm	< 10 µm
SAK_1479_Qu_3	18.8	46.2
SAK_1479_Qu_2	15.1	39.6
SAK_1479_Qu_6	15.1	39.9
SAK_1479_Qu_8	11.3	32.4
SAK_2008_N_38	9.7	18.4
SAK_2008_N_37	9.3	17.5
SAK_2008_FUR_43	8.9	19.1
SAK_1990_Ara_24	8.5	20.5
SAK_2008_FUR_42	8.4	18.1
SAK_2008_AMU_33	7.8	18.5
SAK_2008_N_41	7.5	15.0
SAK_2008_FUR_32	7.5	17.0
SAK_1997_FUR_26	6.7	14.8
SAK_2008_N_39	6.3	13.4
SAK_2000_Har_27	5.7	12.9
SAK_2008_FUR_36	5.6	11.0
SAK_2008_AMU_31	5.5	13.0
SAK_1479_Qu_5	5.4	12.9
SAK_1984_Ara_18	5.4	13.2
SAK_2008_N_40	5.3	10.7
SAK_1984_SVO_17	5.0	11.8
SAK_1479_Qu_1	4.9	11.4
SAK_2000_Kag_29	4.6	10.4
SAK_2009_ N_50	4.6	10.4
SAK_1984_Ara_20	4.5	10.9
SAK_1985_Ara_21	4.4	9.5
SAK_2000_Kag_30	4.3	8.7
SAK_2009_N_49	4.2	10.2
SAK_1914_Qu_9	4.0	9.8
SAK_2000_Kag_28	3.9	8.4
SAK_2008_FUR_35	3.9	8.6
SAK_1992_Ara_25	3.9	9.5
SAK_2009_N_48	3.9	9.4
SAK_2008_FUR_34	3.7	8.2
SAK_1979_Ara_13	3.7	9.1
SAK_2009_N_47	3.7	8.8
SAK_1987_Ara_22	3.4	8.2
SAK_1984_Ara_19	3.1	7.4
SAK_2009_N_45	3.1	7.5
SAK_1479_Qu_4	2.8	6.5
SAK_1988_Ara_23	2.6	6.7
SAK_1983_Ara_15	2.3	5.1
SAK_1974_Har_12	2.0	4.3
SAK_1958_EHS_11	1.9	5.0
SAK_1914_RdC_10	1.7	4.1
SAK_1983_Ara_16	1.6	4.0
SAK_1479_Qu_7	1.5	3.9
SAK_2009_N_44	1.4	3.1
SAK_2009_N_51	1.3	2.6
SAK_1981_Ara_14	1.1	3.0

Table 4. Amount of cristobalite and specific surface area for samples that were examined in detail.

Sample I.D.	Cristobalite (wt. %)	Surface area (m^2 g^{-1})
SAK_1479_Qu_2	1.4	-
SAK_1479_Qu_5	2.1	-
SAK_1914_Qu_9	4.3	-
SAK_1984_SVO_17	4.3	1.3
SAK_1985_Ara_21	4.3	0.5
SAK_1988_Ara_23	4.3	-
SAK_1997_FUR_26	4.3	3.1
SAK_2000_Har_27	5.0	1.5
SAK_2000_Kag_30	5.0	0.5
SAK_2008_AMU_31	2.8	-
SAK_2008_FUR_32	5.7	2.6
SAK_2008_N_38	3.5	3.9


a
Southern
Kyushu
Aira Caldera
Sakurajima
Volcano
Kagoshima
Tarumizu
Kagoshima
Bay
Southern
Kyushu
CHINA
JAPAN
N
0
km
20
b
Aira Caldera
N
Shr
KOP
Kag 30
Kag 28
Kag 29
DoP
RdC
HRT
Uto
SVO
Har
Sakurajima
Volcano
Kur
Ara
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EHS
FUR
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Kagoshima
Tarumizu
Kagoshima
Bay
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0
km
5

Figure 1.

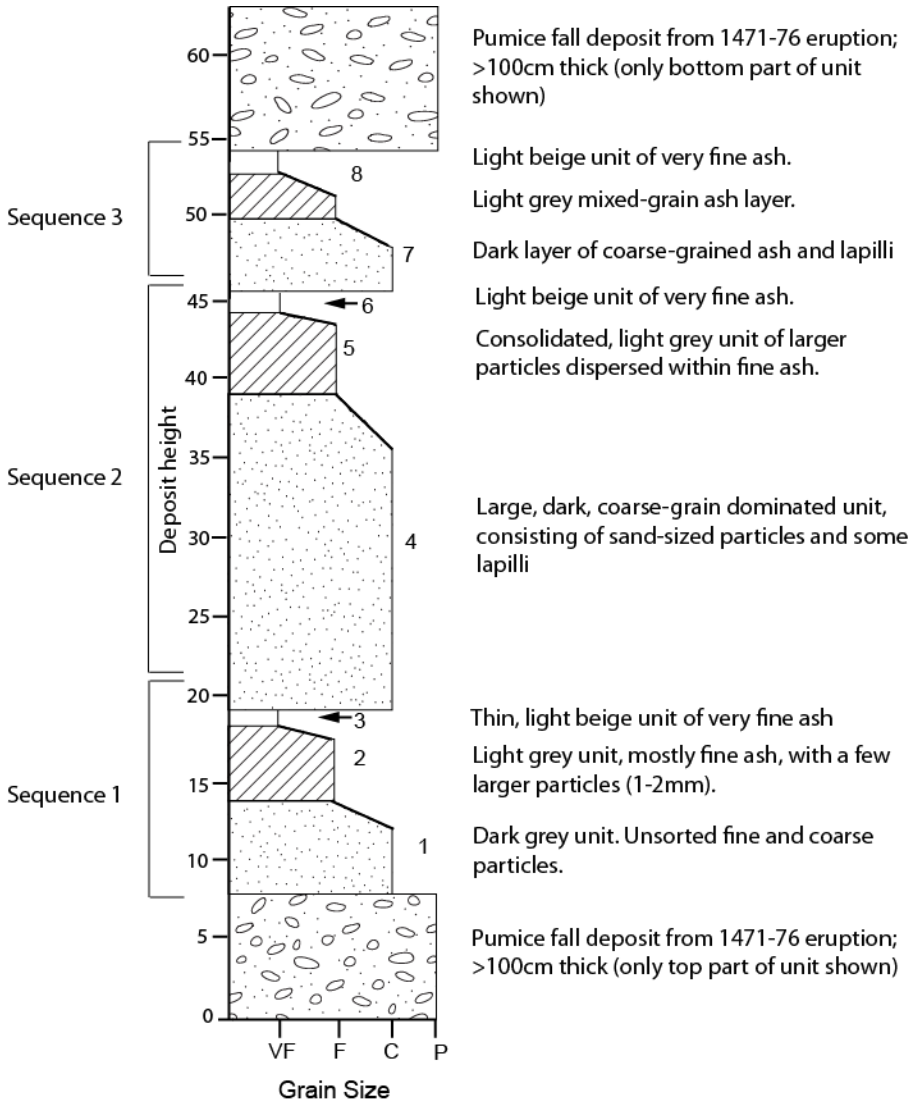
Pumice fall deposit from 1471-76 eruption; >100cm thick (only bottom part of unit shown)
Light beige unit of very fine ash.
Light grey mixed-grain ash layer.
Dark layer of coarse-grained ash and lapilli
Light beige unit of very fine ash.
Consolidated, light grey unit of larger particles dispersed within fine ash.
Large, dark, coarse-grain dominated unit, consisting of sand-sized particles and some lapilli
Thin, light beige unit of very fine ash
Light grey unit, mostly fine ash, with a few larger particles (1-2mm).
Dark grey unit. Unsorted fine and coarse particles.
Pumice fall deposit from 1471-76 eruption; >100cm thick (only top part of unit shown)
Sequence 3
Sequence 2
Sequence 1
Deposit height
60
55
50
45
40
35
30
25
20
15
10
5
0
8
7
6
5
4
3
2
1
VF
F
C
P
Grain Size

Figure 2.

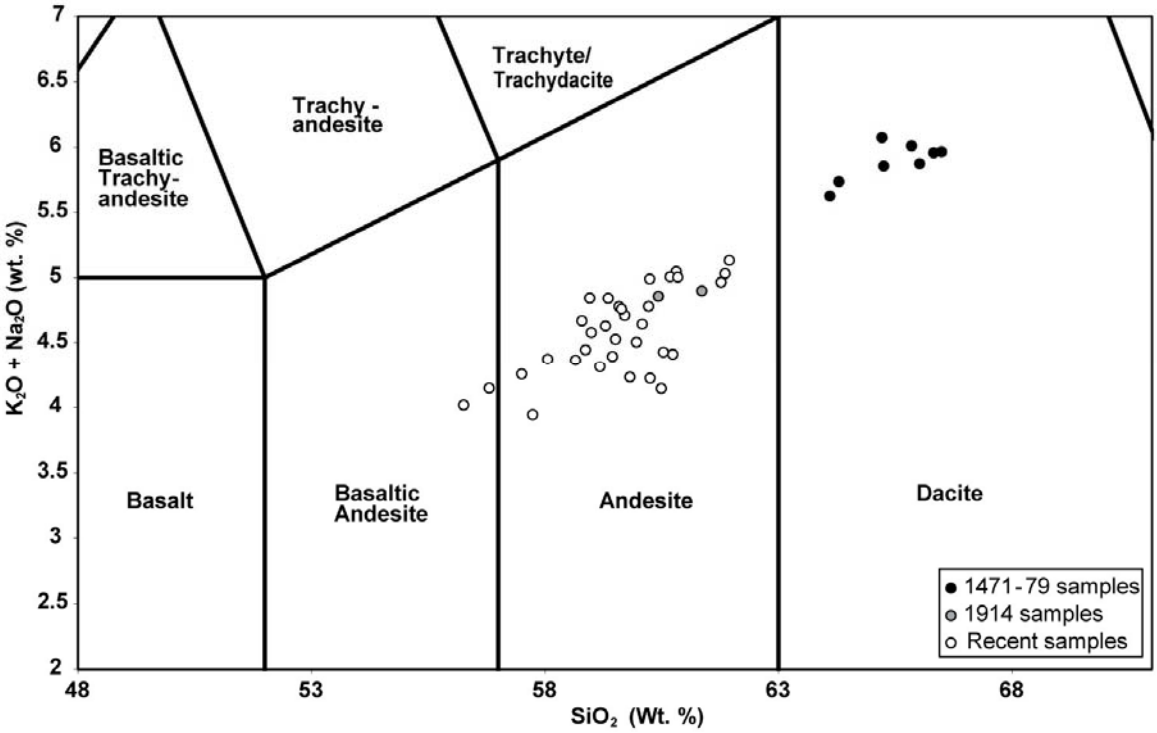
Trachyte/
Trachydacite
Trachy -
andesite
Basaltic
Trachy-
andesite
Basalt
Basaltic
Andesite
Andesite
Dacite
1471-79 samples
1914 samples
Recent samples
$K_2O + Na_2O$ (wt. %)
SiO_2 (Wt. %)
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
48
53
58
63
68

Figure 3.

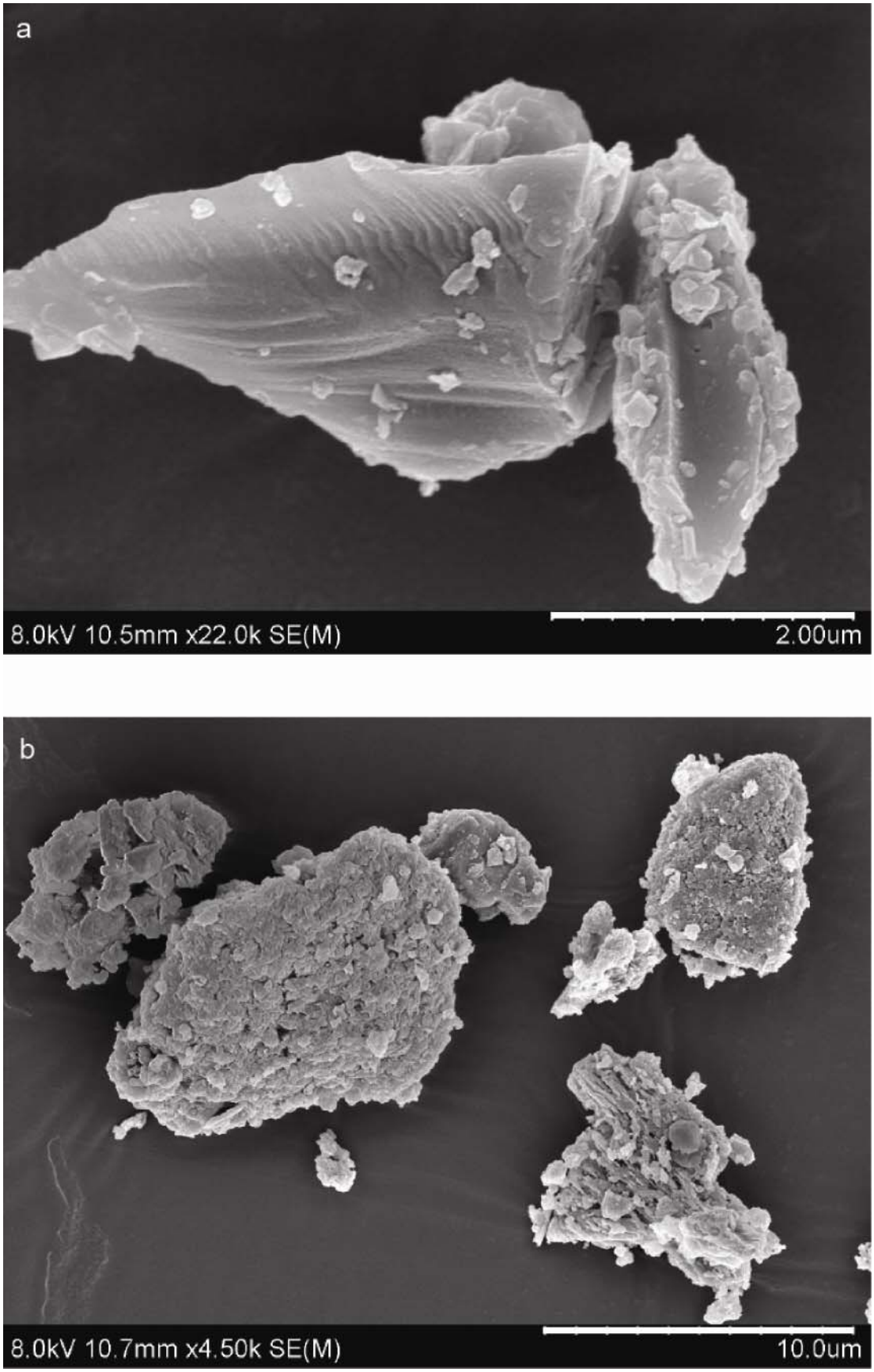

Figure 4.

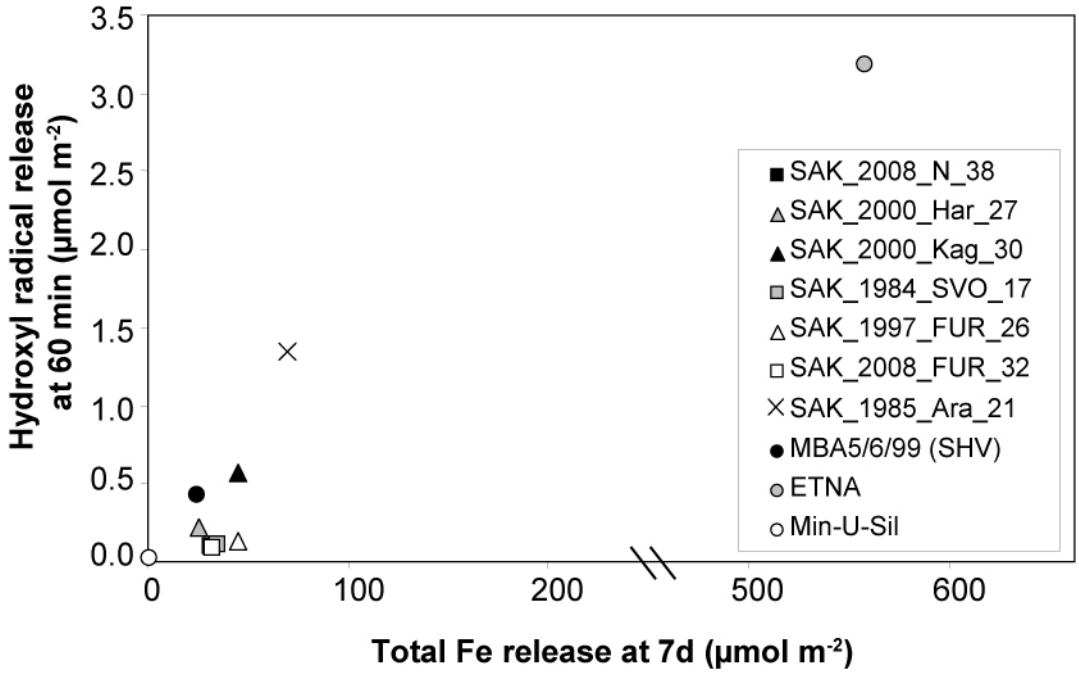
Hydroxyl radical release at 60 min (µmol m-2)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
500
600
Total Fe release at 7d (µmol m-2)
SAK_2008_N_38
SAK_2000_Har_27
SAK_2000_Kag_30
SAK_1984_SVO_17
SAK_1997_FUR_26
SAK_2008_FUR_32
SAK_1985_Ara_21
MBA5/6/99 (SHV)
ETNA
Min-U-Sil

Figure 5.

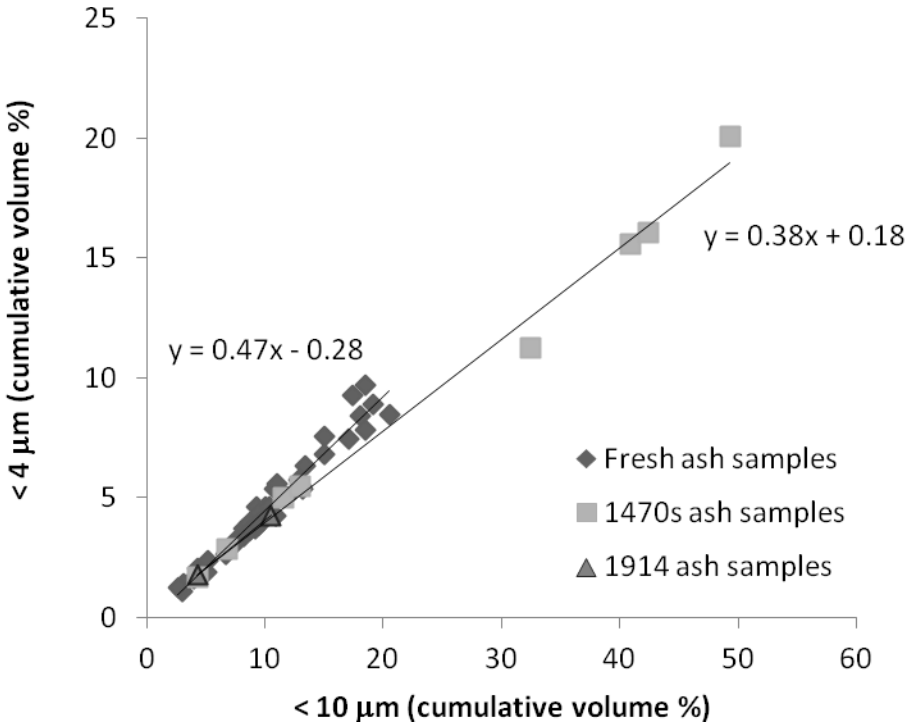
25
20
15
10
5
0
0
10
20
30
40
50
60
< 4 µm (cumulative volume %)
< 10 µm (cumulative volume %)
y = 0.38x + 0.18
y = 0.47x - 0.28
Fresh ash samples
1470s ash samples
1914 ash samples

Figure 6